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TECHNICAL NOTE

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PRELIMINARY STUDY OF THE EFFECTS OF IONIZING RADIATIONS ON PROPELLANTS; THE X-IRRADIATION OF AMMONIA AND HYDRAZINE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

Ammonia and hydrazine were X-irradiated in a preliminary investigation of the effects of ionizing radiations on propellants. A 250-kilovolt, 15-milliampere source was used at room temperature and a distance to provide 90 to 100 roentgens per minute of radiation. Ammonia was irradiated as a vapor at pressures of 100 to 1295 millimeters of mercury with doses of 45 to 104 kiloroentgens of radiation. Less than 1 percent decomposition of ammonia was observed. Liquid ammonia decomposed to the extent of approximately 1 percent with a radiation dose of 115 kiloroentgens. The irradiation of hydrazine vapor at a pressure of 15 millimeters of mercury and a total dose of 590 kiloroentgens resulted in approximately 3 percent decomposition. Both ammonia and hydrazine decompositions involved the formation of nitrogen and possibly hydrogen. In addition to the permanent gases, hydrazine was formed from ammonia and ammonia was formed from hydrazine. All irradiations resulted in the formation of other materials that have not been characterized.

INTRODUCTION

This study of the effects of ionizing radiations on ammonia and hydrazine is part of a broad effort to determine the effects of space environment on the storability of propellants. Specifically, it is planned to learn the overall effect of ionizing radiations on propellants and to determine in a gross manner the chemical nature of the changes that occur. Some data for gaseous and liquid ammonia and for gaseous hydrazine are reported herein. Although the data are preliminary and incomplete, the few observations made so far appear to be worth early mention. The X-ray rates and intensities used are comparable to those that have been observed at a radius as far as about 10^5 kilometers from the earth during quiet-day activity. The total doses used represent the average amount of X-radiation that would be experienced during approximately 1 month in space (refs. 1 to 3).

MATERIALS AND APPARATUS

A commercial grade of ammonia assaying at 99.99 percent minimum purity was used without further purification. Commercial hydrazine, 95, or more, percent pure, was purified to an assay of 99.9 percent, or higher, by a procedure developed at the Lewis center (ref. 4). Irradiations were conducted in borosilicate glassware that had been cleaned with chromic-sulfuric acid. The irradiation cells had a built-in thermocouple and a side arm for attaching a pressure transducer (fig. 1).

The irradiation cells were degassed at 300° C and 10^{-5} millimeter of mercury on a vacuum line and charged with a known quantity of liquid or vapor. Approximately 1.5 milliliters of liquid was used on a 5.5-millimeter inside-diameter cell. The liquid cell (fig. 1(a)) was placed in a bored lead brick, which had a 2-square-centimeter port continuous with the bore near the bottom. In this manner, only the liquid was exposed to the primary X-ray beam. Vapors were irradiated in a cylindrical 500-milliliter bulb (6 by 12 cm; fig. 1(b)). All irradiations were conducted at room temperature.

X-radiation was provided by a machine operating at 250 kilovolts and 15 milliamperes. The irradiation cell was supported in the primary beam at a distance such that after traversing one glass wall thickness the dosage was 100 roentgens per minute (fig. 1). Radiation dosage was determined with a roentgen meter.

The effects of radiation were determined by observation of pressure changes, infrared spectrophotometry, gas chromatography, and potentiometric acid-base and oxidation-reduction titrations. Specific overall amounts of change were obtained by comparing the assay of the initial sample with that of the irradiated sample.

RESULTS AND DISCUSSION

The results from the irradiation of ammonia and hydrazine are summarized in table I. Typical experimental data are described in the following sections of the report.

X-Irradiation of Ammonia Vapor

The X-irradiation of ammonia at a pressure of 100 millimeters of mercury with 45 kiloroentgens of radiation produced undetectable chemical effects; however, a pressure drop of 4 millimeters of mercury was observed. At increased pressure (300 mm Hg) and dosage (94 kr), approximately 0.1 percent of the ammonia was decomposed and the pressure was diminished 6 millimeters of mercury. Nitrogen and possibly hydrogen were qualitatively detected among the products. The infrared spectrogram of the irradiated ammonia was different from that for pure ammonia. It was not possible to account for the difference, nor was it possible to isolate any component responsible for the difference in infrared spectra and the decrease in pressure.

When ammonia at a pressure of 1295 millimeters of mercury was irradiated to the extent of 104 kiloroentgens, approximately 0.5 percent decomposition occurred. The 0.2 milliliter of noncondensable gas that formed contained nitrogen and possibly hydrogen. Attempts to isolate and identify a condensable product other than ammonia or hydrazine were unsuccessful. The product was separated into three parts by vacuum distillation. Infrared spectra were taken on each fraction. The first two fractions were identical with ammonia. Characteristics on the infrared trace from the third part suggested the presence of hydrazine. This fraction contained a component(s) that reduced iodate to iodine; however, not enough of the component(s) was present to obtain a quantitative determination. The reduction of iodate to iodine was used for the quantitative determination of hydrazine.

X-Irradiation of Liquid Ammonia

Approximately 2 grams of liquid ammonia at room temperature was irradiated to the extent of 115 kiloroentgens. Under these conditions, approximately 1 percent of the ammonia was decomposed. The products consisted of 0.5 percent of a condensable product and 0.4 milliliter of a permanent gas. This volume of gas represents a very small percentage of the original ammonia. The condensable product was inconclusively identified as hydrazine on the basis of spot tests and infrared traces. At least 90 percent of the permanent gas was nitrogen; the remainder was possibly hydrogen.

The pressure-time relation for this irradiation is shown in figure 2. The data from two separate irradiations were identical with respect to physical and chemical changes. The pressure decreased during the first 30 minutes (3000 r) followed by an increase during the next hour, after which the slope tends to become constant and continues in this fashion, at least up to the total dose administered. If the X-ray source was turned off once the system was in the constant slope regime, the pressure diminished as shown in figure 2 to a constant value above the initial pressure. This constant value depended on the radiation dose. When the X-ray source was reactivated, the decrease, increase, constant-slope pressure-time relation was observed to reoccur.

X-Irradiation of Hydrazine Vapor

The irradiation of hydrazine vapor at a pressure of 15 millimeters of mercury to the extent of 590 kiloroentgens resulted in the formation of ammonia (approx. 1 percent), a noncondensable gas, nitrogen and possibly hydrogen, (approx. 0.2 percent by volume), and an unidentified product which passed through a trap at -35° C. The initial quantity of hydrazine was decreased by approximately 3 percent. During the course of the irradiation, the pressure was diminished to about one-half its initial value (fig. 3). The irradiated product was allowed to fractionate into traps maintained at 0°, -35°±2°, -90°±2°, and -196° C. The -35° C trap contained only hydrazine (approx. 20 percent of total products by volume). About 75 percent of the irradiated sample was collected in the -90° C trap, which contained hydrazine and other irradiation products. Repeated unsuccessful attempts were made to separate the mixture. The -90° C fraction contained components that were more difficult to oxidize with iodate than was hydrazine. Ammonia was easily isolated in the -196° C trap. Difficulties in obtaining reference spectra for hydrazine, small samples, and inadequate separation techniques all contributed to the incomplete characterization of these products. The pressure-time relation (fig. 3) for the irradiation of hydrazine vapor suggests the formation of larger molecules than hydrazine. The possibility of larger nitrogen chains is remote; however, the formation of hydrazoic acid and azides is a possibility.

SUMMARY OF RESULTS

The X-irradiation of ammonia and hydrazine at room temperature with a 250-kilovolt, 15 milliampere source that provided a radiation of 90 to 100 roentgens per minute gave the following preliminary results:

1. Ammonia gas irradiated at pressures of 100 to 1295 millimeters of mercury with radiations of 45 to 104 kiloroentgens decomposed less than 1 percent.

2. Liquid ammonia decomposed approximately 1 percent with a radiation dose of 115 kiloroentgens.

3. Hydrazine vapor at a pressure of 15 millimeters of mercury and a radiation dose of 590 kiloroentgens decomposed approximately 3 percent.

4. Ammonia and hydrazine decompositions both involved the formation of nitrogen and possibly hydrogen. Hydrazine was also formed from ammonia and ammonia from hydrazine. Materials that were not characterized also resulted from the irradiations.

CONCLUSIONS

The energies and amounts of X-radiation encountered in space flight have small but detectable effects on the physical and chemical properties of ammonia and hydrazine. The effects are sufficiently complicated that additional study is required for proper understanding and for reliable engineering predictions.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, November 22, 1961

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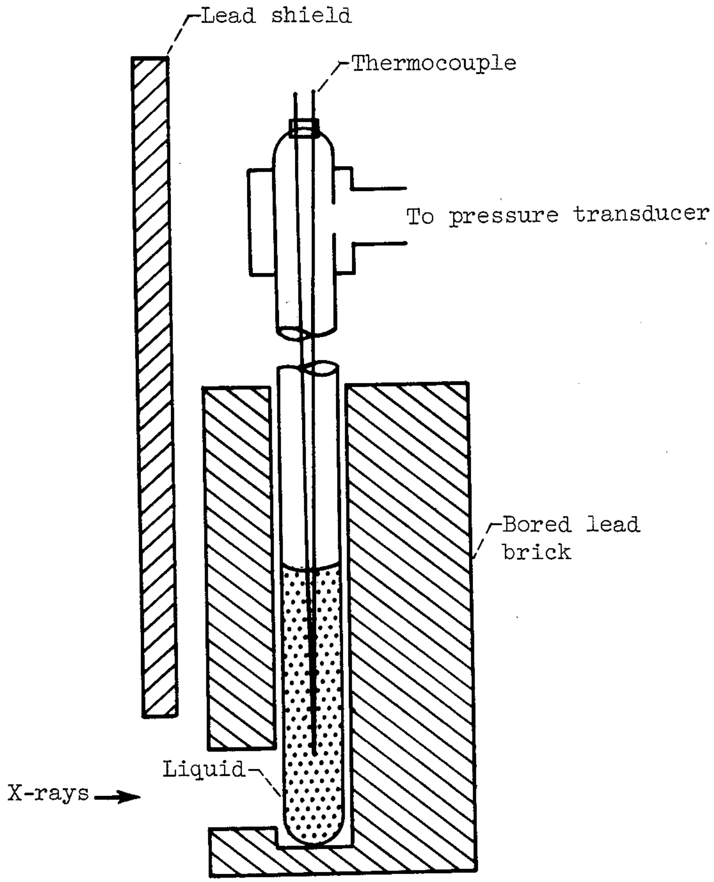
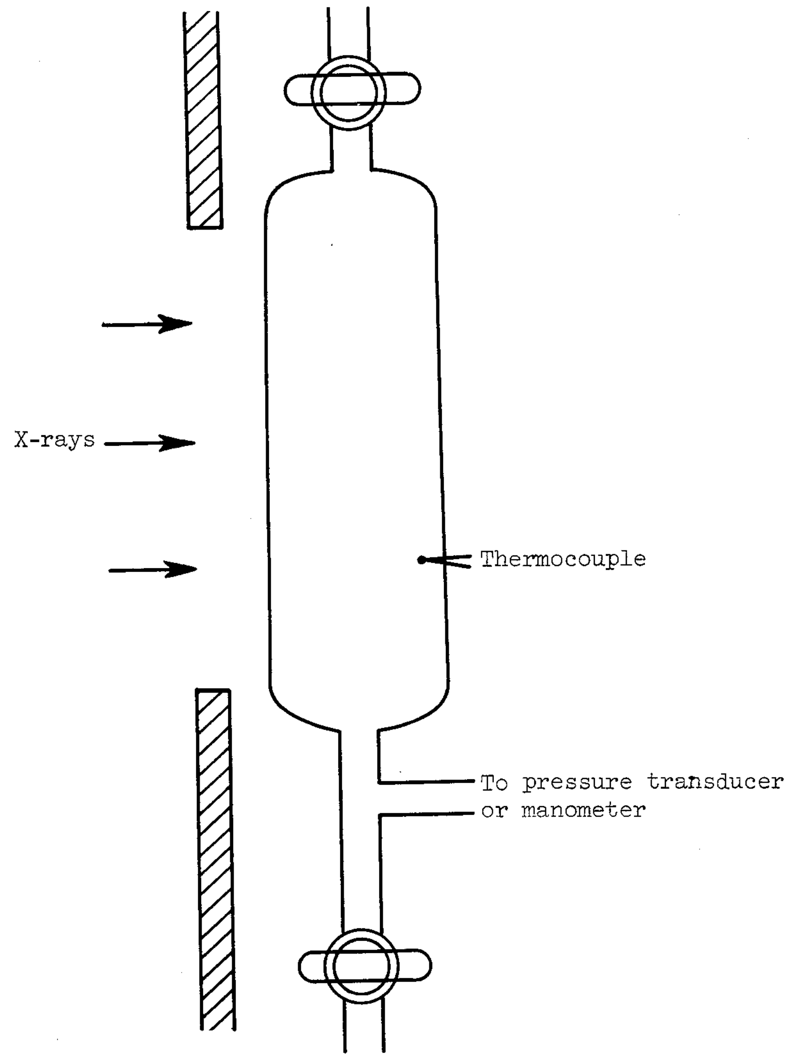
TABLE I. - X-IRRADIATION OF AMMONIA AND HYDRAZINE AT ROOM TEMPERATURE

Substance	Amount, ml	Pressure, mm Hg	Radiation dose, kr	Number of tests	Results
Ammonia vapor	500	100	45	1	Undetectable chemical changes. Pressure diminished by 4 mm Hg.
	500	300	94	2	0.1 percent decomposed. N_2, possibly H_2, and unidentified products were formed.
	500	1295	104	2	0.5 percent decomposed. N_2, possibly H_2, and unidentified products that contain hydrazine were formed.
Ammonia liquid	≈2(g)	----	115	2	Approx. 1 percent ammonia decomposed. 0.4 ml of N_2 and possibly H_2, approx. 0.5 percent of a condensable product possibly containing hydrazine and other unidentified products were formed.
Hydrazine vapor	500	15	590	1	Total hydrazine changed approx. 3 percent: 1 percent volume NH_3, and 0.2 percent volume N_2, and possibly hydrogen. Products that could be condensed with liquid nitrogen but that could not be separated or identified were also formed.



(a) Liquid cell.



(b) Gas cell.

Figure 1. - Borosilicate glass cells used to irradiate ammonia and hydrazine.

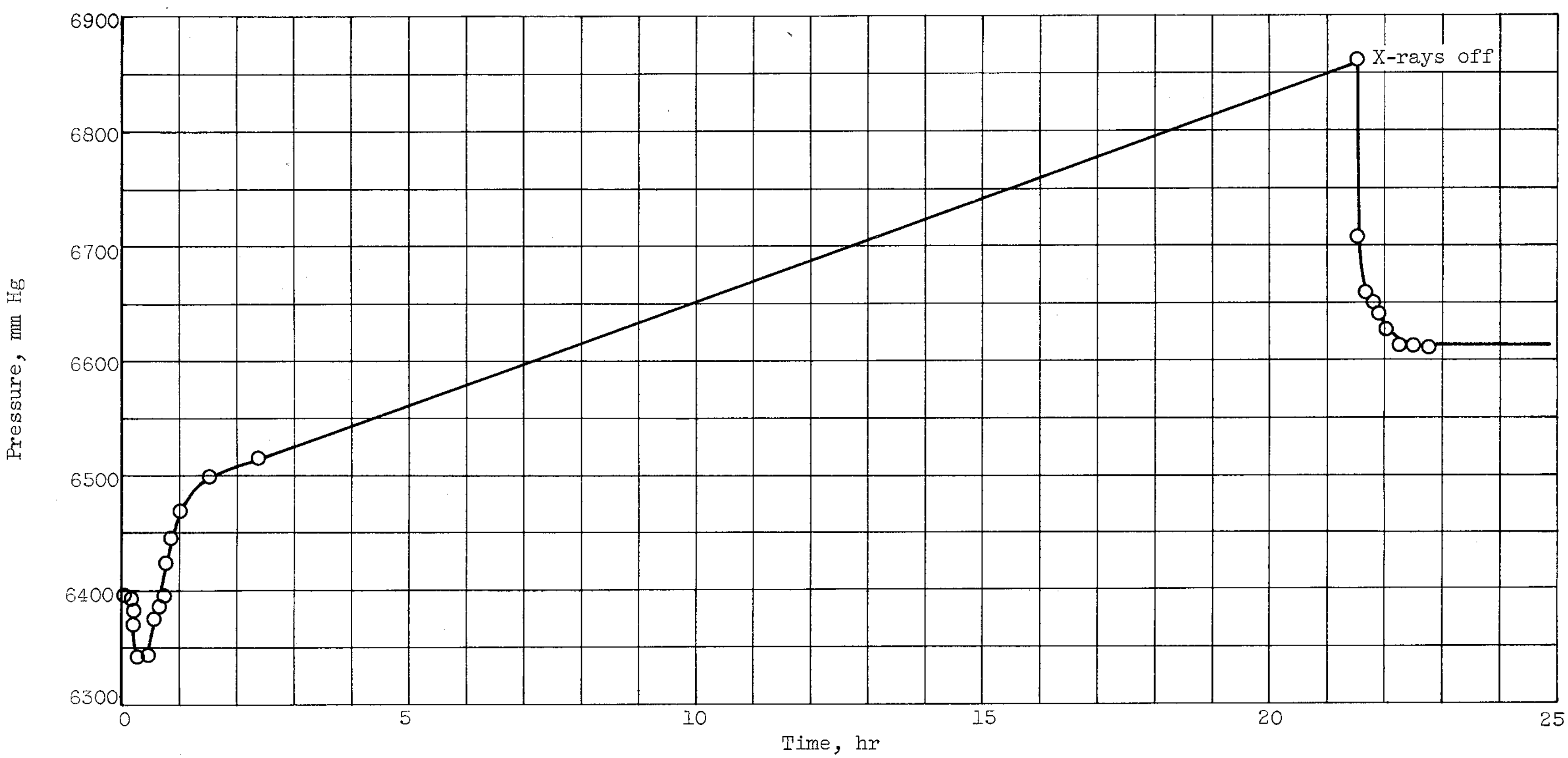


Figure 2. - X-irradiation of liquid ammonia at room temperature. Total radiation dose, 115 kiloroentgens; source, 250 kilovolts, 15 milliamperes.

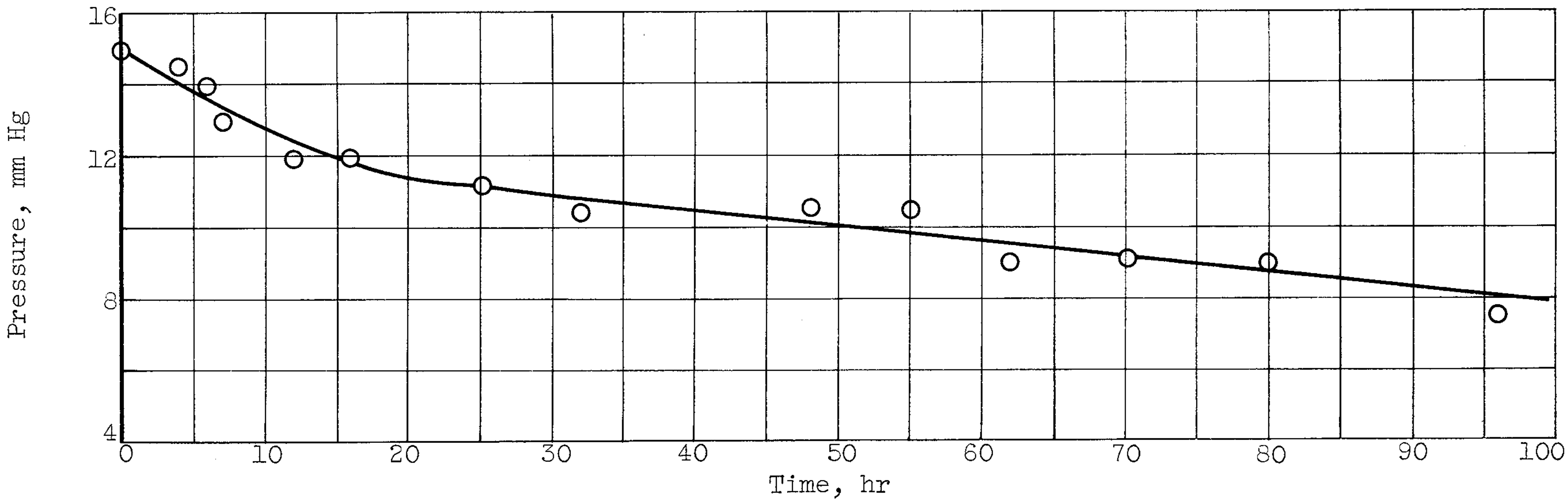


Figure 3. - X-irradiation of hydrazine vapor. Total radiation dose, 590 kiloroentgens; source, 250 kilovolts, 15 milliamperes.

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